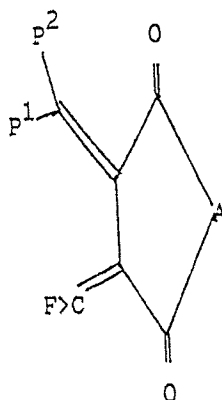


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(54) Title: NOVEL PHOTOACTIVE COMPOUNDS



(III)

(57) Abstract

Photoactive compounds having general formulae (III) are provided in which A represents oxygen or NR¹ wherein R¹ represents hydrogen, alkyl having 1 to 20 carbon atoms, cycloalkyl having 5 to 12 carbon atoms, aralkyl having 7 to 9 carbon atoms, aryl having 6 to 14 carbon atoms, which may be substituted with one or more halogen or alkoxy groups having 1 to 20 carbon atoms, or alkaryl having 7 to 22 carbon atoms; P¹ represents a 5-substituted-3-furyl, 3-thienyl, or 3-pyrrolyl group, said 5-substituted-3-furyl, 3-thienyl and 3-pyrrolyl groups being unsubstituted or substituted in the 2-position, said optional 2-substituents being selected from alkyl groups having 1 to 20 carbon atoms and aralkyl groups having 7 to 12 carbon atoms, and said 5-substituents being selected from (i) aryl groups having 6 to 14 carbon atoms, substituted with a group of the formula -NR₇R₈ wherein R₇ and R₈ each represent hydrogen or alkyl having 1 to 20 carbon atoms or together with the nitrogen atom to which they are attached represent a 1-pyrrolidine, a 1-piperidine, or a morpholine group, and (ii) heterocyclic groups selected from 2-thienyl, 3-thienyl, 2-furyl and 3-furyl groups, said last-mentioned 2-thienyl, 3-thienyl, 2-furyl and 3-furyl groups being unsubstituted or substituted by one or more C₁₋₃ alkyl groups or halogen atoms; P² represents alkyl having 1 to 20 carbon atoms, cycloalkyl having 3 to 12 carbon atoms, aralkyl having 7 to 9 carbon atoms, aryl having 6 to 14 carbon atoms which may be unsubstituted or substituted with one or more halogen atoms, or alkaryl having 7 to 22 carbon atoms; and F>C = represents a substituted methylene group, having at least two carbon atoms.

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NOVEL PHOTOACTIVE COMPOUNDS

This invention relates to a novel class of photoactive compounds and to processes for their production.

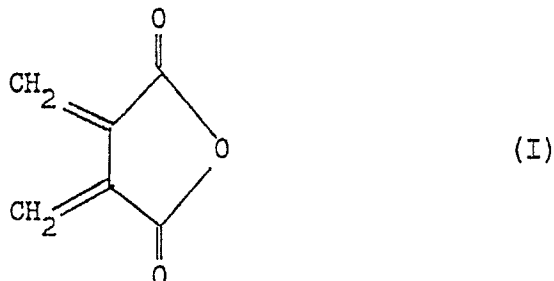
As used herein, the expression "photoactive compound" is defined as a compound which undergoes a structural change (hereinafter referred to as a "photoactive change") when subjected to electromagnetic radiation of a selected wavelength or wavelengths and undergoes a reversal to its original structure when subjected to thermal energy or to electromagnetic radiation of another wavelength and wherein the distinct structural forms interact differently with electromagnetic radiation. For example they may have different spectral absorption characteristics which can manifest themselves by the structural forms having different observable colours and often different dispersivities and refractive indices.

Photoactive compounds as defined above which undergo major colour changes on conversion between their respective structural forms are referred to as "photochromic compounds".

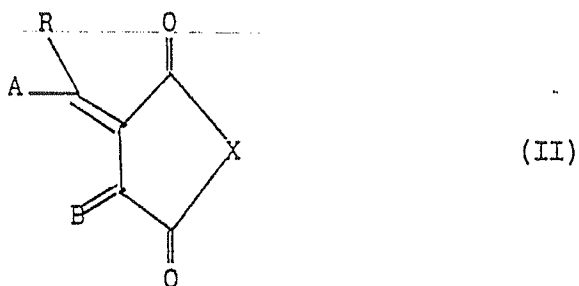
Photochromic compounds have a wide range of uses, e.g. in the manufacture of image and data recording media and in display systems.

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An important class of photochromic compounds is based on bismethylenesuccinic anhydride or "fulgide" (I).



Such compounds are exemplified by those described in GB-1442628, GB 1464603, GB 2002752 and US 4220708. Thus, for example US-4220708 describes and claims a class of compounds of the formula

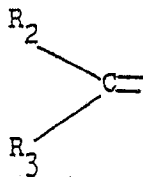


wherein X represents oxygen or NR_6 , R_6 being hydrogen or an alkyl, aryl or aralkyl group;

R represents an alkyl or aryl group;

A represents a 3-furyl, 3-thienyl, 3-benzofuryl or 3-benzothienyl group; and

B represents an adamantylidene group or the grouping



in which R_2 and R_3 independently represent an alkyl, aryl, or a heterocyclic group containing a 3-furyl or 3-thienyl ring or one of R_2 and R_3 represents hydrogen and the other represents an alkyl or aryl group.

By appropriate selection of substituents on the 3-furyl, 3-thienyl, 3-benzofuryl and 3-benzothieryl groups represented by A and by appropriate selection of groups X, R and B, photochromic compounds having a range of properties may be produced. Compounds of formula II in which B represents an adamantylidene group are preferred as they have a high quantum efficiency for bleaching of their coloured forms. They further show good thermal stability and the ability to undergo a large number of colour change cycles without substantial deterioration in the character of the absorption spectra as a result of the formation of so-called "fatigue products" of irreversible side reactions.

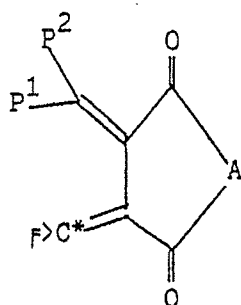
However the preferred compounds of US 4220708 in which B represents adamantylidene are expensive to produce owing to the high cost of adamantanone used as a starting material. Also, for the known compounds and their coloured forms, only a relatively restricted number of characteristic wavelengths may be used to induce a photochromic change in structure and compounds having only a relatively restricted range of characteristic absorption wavelengths are available. These disadvantages impose limitations, where for example it is wished to mass-produce data storage media economically, or where it is necessary to produce a photochromic

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compound having optical characteristics which match the characteristic wavelengths of available sources of electromagnetic radiation, e.g. semi-conductor diode lasers.

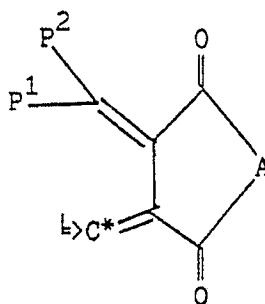
A further difficulty with many known compounds is their limited solubility in organic solvents and limited capacity to form solid solutions with plastics materials. Photochromic compounds having a higher solubility than known compounds would be desirable in many fields. For example in the production of security printing inks and varnishes it is desirable for the components of the inks to be soluble in the liquid ink base. In other methods of printing, higher solubility would enhance the formulation of solid solutions in plastics materials. Similarly in order to produce thin, uniform coatings on data storage media, it is advantageous to use a coating fluid containing a photochromic compound in the dissolved state. Currently available photochromic materials of limited solubility fail to satisfy these criteria.

Our International Patent Application No PCT/GB89/00155 describes and claims photochromic compounds having the general formula



(IIIa)

or



(IIIb)

wherein the substituents P^1 , P^2 , $f>C^*$, $h>C^*$ and A are defined as follows:

A represents oxygen or NR^1 wherein R^1 represents hydrogen, alkyl having 1 to 20 carbon atoms, cycloalkyl having 5 to 12 carbon atoms, aralkyl having 7 to 9 carbon atoms, aryl having 6 to 14 carbon atoms, which may be substituted with one or more halogen or alkoxy groups having 1 to 20 carbon atoms, or alkaryl having 7 to 22 carbon atoms;

P^1 represents a 3-furyl, a 3-thienyl, a 3-pyrrolyl, a 3-benzofuryl or a 3-benzothienyl group, each of which may be unsubstituted or substituted by substituents defined below;

P^2 represents a C_{1-20} alkyl, a C_{3-12} cycloalkyl, a C_{7-9} aralkyl, a C_{6-14} aryl (which may be unsubstituted or substituted by one or more halogen atoms) or a C_{7-22} alkaryl group; and

$f>C^*$ and $h>C^*$ represent a substituted or unsubstituted bridged polycyclic hydrocarbon residue containing from 7 to 20 carbon atoms in a polycyclic system, said residue having a plane of asymmetry which is parallel to the plane which includes the single bonds extending from carbon atom C^* and the anhydride or imide ring, any substituents on the bridged polycyclic hydrocarbyl residue being selected from alkyl groups having 1 to 4 carbon atoms, halogen atoms and hydroxy groups.

According to the aforementioned International Application, the optional substituents on the 3-furyl, 3-thienyl and 3-pyrrolyl groups may be in the 2- and/or 5-positions.

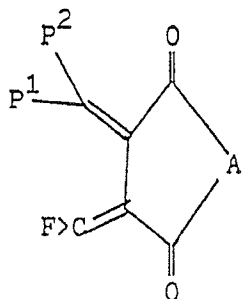
The optional 5-substituents are selected from

- (i) C_{1-20} alkyl groups,
- (ii) C_{3-12} cycloalkyl groups,
- (iii) C_{3-12} cycloalkenyl groups,
- (iv) C_{6-14} aryl groups, which are unsubstituted or substituted
 - (a) with one or more alkoxy groups,
 - (b) with a group of the formula $-NR_7R_8$, wherein R_7 and R_8 each represent hydrogen or C_{1-20} alkyl or together with the nitrogen to which they are attached represent a 1-pyrrolidine, a 1-piperidine or a 1-morpholine group), or
 - (c) with one or more halogen atoms,
- (v) C_{7-12} aralkyl groups,
- (vi) halogen atoms, and
- (vii) heterocyclic groups selected from 2-thienyl, 3-thienyl, 2-furyl and 3-furyl groups, said heterocyclic groups (vii) being unsubstituted or substituted by one or more C_{1-3} alkyl groups or halogen atoms.

We have now found that a class of compounds of related structure to the aforementioned compounds of formulae (IIIa) and (IIIb) have particularly advantageous properties and particularly are capable of undergoing photoactive change to coloured forms with a range of colours that extends beyond that obtainable with the previously produced compounds. In particular, the new class of compounds according to the invention exhibit particularly advantageous bathochromic shifts and hyperchromic effects.

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According to the present invention there is provided a photoactive compound having the general formula



(III)

in which

A represents oxygen or NR¹ wherein R¹ represents hydrogen, alkyl having 1 to 20 carbon atoms, cycloalkyl having 5 to 12 carbon atoms, aralkyl having 7 to 9 carbon atoms, aryl having 6 to 14 carbon atoms, which may be substituted with one or more halogen or alkoxy groups having 1 to 20 carbon atoms, or alkaryl having 7 to 22 carbon atoms;

P¹ represents a 5-substituted 3-furyl, 3-thienyl, or 3-pyrryl group, said 5-substituted 3-furyl, 3-thienyl and 3-pyrryl groups being unsubstituted or substituted in the 2-position, said

optional 2-substituents being selected from alkyl groups having 1 to 20 carbon atoms and aralkyl groups having 7 to 12 carbon atoms, and said 5-substituents being selected from (i) aryl groups having 6 to 14 carbon atoms, substituted with a group of the formula $-NR_7R_8$ wherein R_7 and R_8 each represent hydrogen or alkyl having 1 to 20 carbon atoms or together with the nitrogen atom to which they are attached represent a 1-pyrrolidine, a 1-piperidine, or a morpholine group, and (ii) heterocyclic groups selected from 2-thienyl, 3-thienyl, 2-furyl and 3-furyl groups, said last-mentioned 2-thienyl, 3-thienyl, 2-furyl and 3-furyl groups being unsubstituted or substituted by one or more C_{1-3} alkyl groups or halogen atoms;

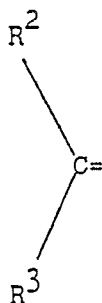
P^2 represents alkyl having 1 to 20 carbon atoms, cycloalkyl having 3 to 12 carbon atoms, aralkyl having 7 to 9 carbon atoms, aryl having 6 to 14 carbon atoms which may be unsubstituted or substituted with one or more halogen atoms, or alkaryl having 7 to 22 carbon atoms; and

$F>C=$ represents a substituted methylene group, having at least two and preferably from 2 to 20 carbon atoms.

In a preferred class of compounds, $F>C=$ is an unsubstituted hydrocarbyl radical. However the invention also includes compounds in which wherein $F>C=$ is a substituted hydrocarbyl radical, e.g. one having one or more substituents selected from hydroxy, oxo, halogen, $-SO_3H$ and $COOH$.

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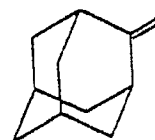
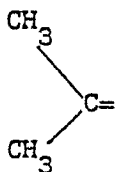
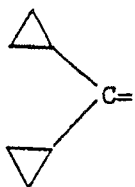
Specific examples of groups $F>C=$ include those having the structure



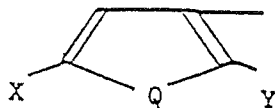
in which R^2 and R^3 independently represent hydrogen, C_{1-20} alkyl, C_{6-14} aryl, C_{7-12} alkaryl, C_{7-12} aralkyl, C_{3-12} cycloalkyl, heterocyclic group containing 5-12 atoms arranged in one, two or three rings (including bicyclic structures) and having at least one hetero-atom selected from N, S and O (with the proviso that R_2 and R_3 are not both hydrogen), or R^2 and R^3 together represent a divalent cyclic or polycyclic hydrocarbyl group.

One or more of said alkyl, aryl, alkaryl, aralkyl, cycloalkyl, heterocyclic or polycyclic groups representing R^1 and R^2 may be substituted for example by one or more of the substituents referred to above in relation to $F>C=$.

In a preferred class of compounds, symbol $F>C$ represents



From amongst the definition of P^1 above, the following structures are preferred.

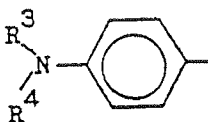


where Q is oxygen or sulfur,

Y is C_{1-4} alkyl

X is selected from;

(a) a 4-substituted phenyl group to the formula



wherein R^3 and R^4 each represents a C_{1-4} alkyl group or together with the nitrogen atom to which they are attached form a pyrrolide, piperidine or morpholine group.

(b) a 2-thiophene group optionally substituted in the 3- and/or 5-positions by a C_{1-4} alkyl group.

(c) a 3-thiophene group optionally substituted in the 2-and/or 5-position with C_{1-4} alkyl groups.

Examples of compounds according to the invention which are preferred are those in which P¹ represents:

5-(p-diethylaminophenyl)-2-methyl-furan-3-yl,
5-(p-piperidinophenyl)-2-methyl-furan-3-yl,
5-(p-pyrrolidinophenyl)-2-methyl-furan-3-yl,
5-(2-thienyl)-2-methyl-furan-3-yl,
5-(3-thienyl)-2-methyl-furan-3-yl,
5-(2,5-dimethyl-3-thienyl)-2-methyl-furan-3-yl,
5-(2-thienyl)-furan-3-yl, or
5-(2,5-dimethyl-3-thienyl)-furan-3-yl.

As indicated above, the compounds of formulae (III) are photoactive. That is to say compounds of formulae (III) are capable of undergoing a structural change when subjected to electromagnetic radiation of a selected wavelength or wavelengths and undergo a reversal to their original form when subjected to thermal energy or to electromagnetic radiation of another wavelength.

The use of the compounds of formula III in the manufacture of image and data recording media thus forms a further aspect of the invention.

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The compounds of the invention of formula (III) may be prepared by the Stobbe condensation from a lower dialkyl succinates, e.g. diethyl succinate.

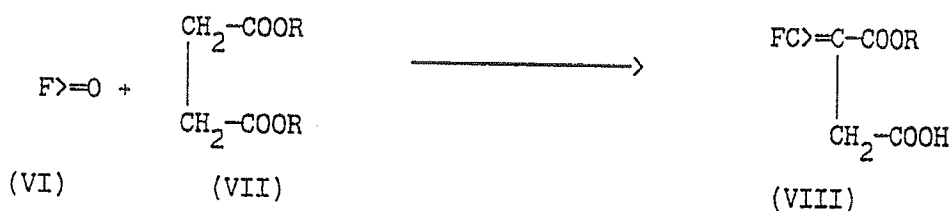
Advantageously a modification to conventional Stobbe reaction conditions is employed which will be discussed in further detail below and forms a further aspect of the invention.

Various sequences of reaction may be used, e.g. the sequences referred to as "Sequence 1" and "Sequence 2" below.

The production of compounds of formulae (III) by Sequence 1 is as follows:

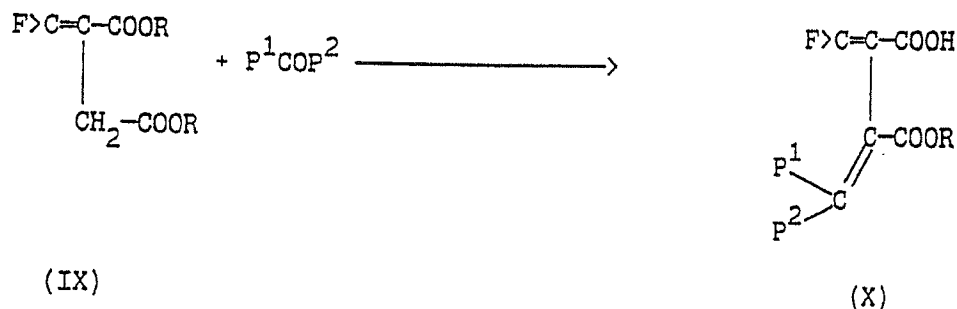
Sequence 1

In a first step a ketone (VI) is reacted with a di-lower alkyl succinate (VII, R = lower C₁₋₄ alkyl)



to yield condensation product VIII. The reaction is carried out in the presence of a basic catalyst e.g. as described in more detail below.

Condensation product VIII is esterified to form the diester (IX, R = lower alkyl) which is then reacted with a ketone P¹COP²

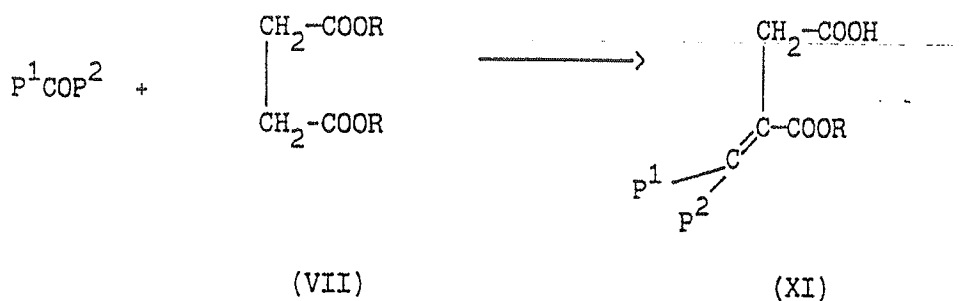


Half-ester X is hydrolysed to form the corresponding dicarboxylic acid and then converted into the desired compound of formula III by treatment with a dehydrating agent (e.g. an acyl halide) to form a compound in which A is oxygen, which in turn can be converted into a compound in which A represents NR^1 by reacting with an amine H_2NR^1 .

The production of compounds according to the invention by Sequence 2 will now be described.

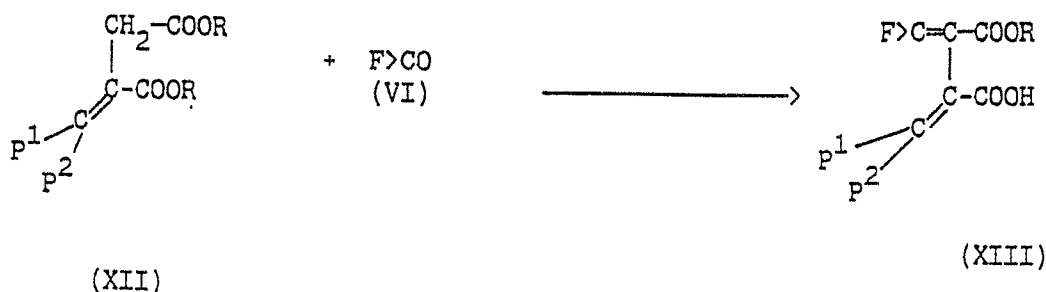
Sequence 2

In a first step, a ketone P^1COP^2 may be reacted with a di-lower alkyl succinate (VII, R=lower C_{1-4} alkyl)



to yield a condensation product XI. The reaction is carried out in the presence of a basic catalyst, e.g. as described in more detail below.

Condensation product XI is esterified to form the diester (XII, R=lower alkyl) which is then reacted with a ketone (VI).



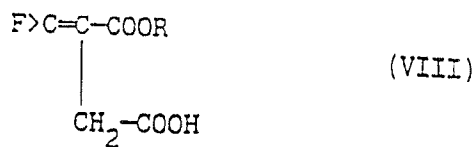
Half-ester (XIII) is hydrolysed to form the corresponding dicarboxylic acid and then converted into the desired compounds IIIa and IIIb as described above.

Conventionally, in carrying out a Stobbe condensation in which a ketone is condensed with a dialkyl succinate, the reaction is generally carried out in ethanol or t-butanol, using sodium ethoxide or potassium t-butoxide as catalyst respectively. Alternatively the reaction has been carried out in toluene, using sodium hydride plus a trace of ethanol, as catalyst.

Yields obtainable with existing reaction media and catalysts can be low, particularly when the reactants are sterically hindered. As indicated in the aforementioned International Patent Application No. PCT/GB89/00155, it has unexpectedly been found that a particular catalyst/reaction medium combination gives improved high yields.

Thus according to this procedure, a condensation product between a lower alkyl ester of succinic acid (or a methylene derivative of succinic acid in which at least one of the hydrogen atoms of the methylene groups is replaced by a substituent which does not interfere with the reaction) and a ketone, is formed by reacting said ester and said ketone in the presence of an aromatic hydrocarbon, preferably toluene, and an alkali metal alkoxide, preferably potassium t-butoxide.

Applied to the production of compounds according to the invention, (Sequence 1) there is provided a process for producing a compound of formula



wherein R and F>C are as defined above which comprises reacting a di-lower alkyl succinate of general formula

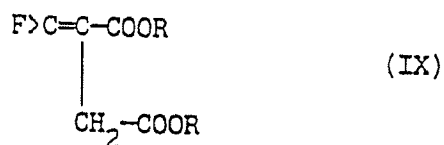


wherein R is as defined above with a ketone of formula



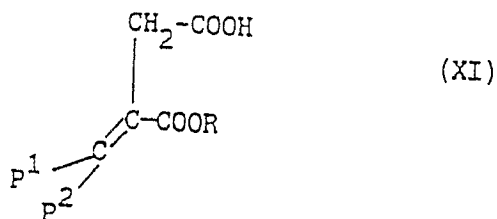
wherein F>C is as defined above, characterised in that the reaction is carried out in a reaction medium comprising toluene and in the presence of potassium t-butoxide as catalyst.

The resulting compound of formula (VIII) may then be esterified to form a compound of formula IX



and reacted with a ketone of formula P^1COP^2 , wherein P^1 and P^2 are as defined above to form a compound of formula (III).

According to (Sequence 2) there is provided a process for producing a compound of formula



wherein R, P¹ and P² are as defined above which comprises reacting a di-lower alkyl succinate of general formula

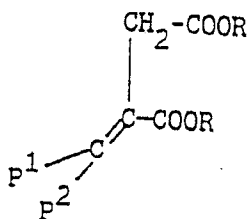


wherein R is as defined above with a ketone of formula



wherein P¹ and P² are as defined above, characterised in that the reaction is carried out in a reaction medium comprising toluene and in the presence of potassium t-butoxide as catalyst.

The resulting compound of formula (VIII) may then be esterified to form a compound of formula IX



and reacted with a ketone of formula F>CO (XIII), to form a compound of formula (III).

The production of photoactive compounds according to the invention, and their optical properties will now be described in more detail in the following Examples.

Example 1

E- α -5-(p-Diethylaminophenyl)-2-methyl-3-furylethylidene(isopropylidene) succinic anhydride (VIa, Z = diethylamino)

The ketone (I, R = diethylamino) (5 g, 18 mM) was added to a solution of potassium t-butoxide (2.38 g, 21 mM) in tetrahydrofuran (75 ml) and the mixture cooled below 5°C. Diethyl isopropylidene succinate (2a, R = ethyl) (4.74 g, 22 mM) in tetrahydrofuran (25 ml) was added dropwise with stirring. When the addition was complete, the reaction mixture was stirred at room temperature for 1 hour. Water (25 ml) was added and tetrahydrofuran and water were removed under reduced pressure. Water (25 ml) was added and the aqueous solution was extracted with ether to remove neutral biproducts. The aqueous layer was very carefully acidified to liberate the half-ester (IIa, Z = diethylamino) which was extracted with chloroform and dried over anhydrous magnesium sulphate. The extract was filtered and the solvent removed. The residual light brown oil of the half ester was hydrolysed by boiling with 10% ethanolic potassium hydroxide (20 ml) for 1 hour. The mixture was cooled, water (25 ml) was added, and most of the ethanol removed by distillation under reduced pressure. The solution was very carefully acidified with 5 M hydrochloric acid to liberate the diacid (IIIa, Z = diethylamino) which was extracted with chloroform, dried over anhydrous magnesium sulphate and filtered. The solvent was removed from the filtrate to leave the diacid which was converted into the fulgides (IVa, Z = diethylamino) (both isomers) by treatment with acetyl chloride (20 ml) followed by removal of the excess acetyl chloride under reduced pressure. The mixture of E- and Z-fulgides were recrystallised from ethanol.

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Example 2

E- α -5-(p-Piperidinophenyl)-2-methyl-3-furylethylidene (isopropylidene) succinic anhydride (IVa, Z = diethylamino)

The reaction was carried out as for Example 1 except that ketone (I, Z = piperidino) (5 g) was used in place of ketone (I, Z = diethylamino).

Example 3

E- α -5-(p-Pyrrolidinophenyl)-2-methyl-3-furylethylidene(isopropylidene) succinic anhydride (IVa, Z = pyrrolidino)

The reaction was carried out as for Example 1 except that ketone (I, Z = pyrrolidino) (5 g) was used in place of ketone (I, Z = diethylamino).

The coloured form in toluene after irradiation of the (E) fulgide (IVa, Z = pyrrolidino) has a molar extinction coefficient of over $26,250 \text{ dm}^3 \text{ cm}^{-1} \text{ mol}^{-1}$, at 588 nm, the maximum of the absorption band in the visible region.

Example 4

E- α -5-(p-Diethylaminophenyl)-2-methyl-3-furylethylidene(adamantylidene) succinic anhydride (IVd, Z = diethylamino)

The reaction was carried out as for Example 1 except that diethyl adamantylidene succinate (6 g) (2d, R = ethyl) was used in place of diethyl isopropylidene succinate (2a, R = methyl).

The coloured form in toluene after irradiation of the (E)-fulgide (IVd, Z = diethylamino) has a molar extinction coefficient of over $18,500 \text{ dm}^3 \text{ cm}^{-1} \text{ mol}^{-1}$ at 612 nm, the maximum of the absorption band in the visible region.

Example 5

E- α -5-(2-thienyl)-2-methyl-3-furylethylidene(isopropylidene) succinic anhydride (5a, X = 2-thienyl).

The ketone (1, X= 2-thienyl) (10 g, 48 mM) was added to a solution of potassium t-butoxide (6.46 g, 58 mM) in tetrahydrofuran (250 ml). The mixture was cooled below 5°C and diethyl isopropylidene succinate (2a, R = ethyl) (10.28 g, 48 mM) was added dropwise with stirring. After 1 hour, the reaction mixture was allowed to warm up to room temperature and was stirred for a further 12 hours. Most of the tetrahydrofuran was removed under reduced pressure and ether (100 ml) was added. The ethereal solution was extracted with water and the combined aqueous extracts were acidified with conc. hydrochloric acid. The liberated half-ester (3a, X = 2-thienyl, R = ethyl) was extracted with ether. The ether layer was dried over anhydrous magnesium sulphate and filtered. Solvent was removed from the filtrate and the residual dark oil containing the half-ester (14.7 g) was hydrolysed with 10% ethanolic potassium hydroxide (150 ml). On cooling, the dipotassium salt of the diacid (4a, X= 2-thienyl) crystallised. The salt was filtered off, dissolved in water and acidified with concentrated hydrochloric acid, giving the diacid in 68% yield. The diacid (5.14 g, 15 mM) was dissolved in ether (150 ml) and treated with acetyl chloride (10 ml). Excess acetyl chloride and ether were removed by distillation and the E-fulgide (5a, X = 2-thienyl) was crystallised from a mixture of ethanol, acetic acid, and ethyl acetate, giving yellow crystals 182-4°C.

Example 6

E- α -5-(3-thienyl)-2-methyl-3-furylethylidene(isopropylidene) succinic anhydride (5a, X = 3-thienyl).

The reaction was carried out as for example 5 except that the ketone (1, X= 3-thienyl) was used in place of ketone (1, X= 2-thienyl).

The Z-isomer of the product was obtained as colourless crystals from ethanol m.p. 149-150°C.

Example 7

E- α -5-(2,5-dimethyl-3-thienyl)-3-furylethylidene(isopropylidene) succinic anhydride (5a, X = 2,5-dimethyl-3-thienyl).

The reaction was carried out as for example 5 except that the ketone (1, X = 2,5-dimethyl-3-thienyl) was used in place of ketone (1, X = thienyl).

The product was obtained as near colourless crystals, m.p. 164-166°C.

Example 8

E- α -5-(2-thienyl)-3-furylethylidene(dicyclopropylmethylene) succinic anhydride (5b, X = 2-thienyl).

The reaction was carried out as for example 5 except that dimethyl dicyclopropylmethylene succinate (2b, R = methyl) was used in place of diethyl isopropylidene succinate (2a, R = ethyl).

Example 9

E- α -5-(2-thienyl)-3-furylethylidene (adamantylidene)succinic anhydride (5c, X = 2-thienyl).

The reaction was carried out as for example 5 except that dimethyl adamantylidene succinate (2c, R = methyl) was used in place of diethyl isopropylidene succinate (2a, R = ethyl).

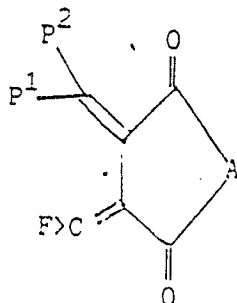
Example 10

E- α -5-(2,5-dimethyl-3-thienyl)-3-furyl ethylidene(dicyclopropylmethylene) succinic anhydride (5b, X = 2,5-dimethyl-3-thienyl).

2,5-Dimethyl-3-acetylthiophene (1, X = 2,5-dimethyl-3-thienyl) (50 g, 0.33 M) and dimethyl dicyclopropylmethylene succinate (2c, R = methyl) (74 g, 0.33 M) in dry toluene (100 ml) was added dropwise, with stirring, over 1 hour to potassium t-butoxide (60 g, 0.53 M) in dry toluene (500 ml) at 0°C. After 1.5 hours water (1 l) was added and the aqueous layer separated. Acidification (5M HCl) and extraction with ether (2 x 300 ml) gave a solution which was dried (Mg SO₄) and filtered. Removal of solvent from the filtrate gave a near quantitative yield of crude half-ester (3b, X = 2,5-dimethyl-3-thienyl). The half-ester was hydrolysed with KOH (50 g) in isopropanol (500 ml) by boiling for 1 hour. The reaction mixture was left overnight. The potassium salt of the diacid was filtered off, washed with acetone (1 l) and suspended in dry toluene (500 ml) and Na₂CO₃ (20 g) added. Acetyl chloride (50 ml) was added dropwise with stirring over 1 hour. After a further 30 min, the solution was filtered, and the solid residue was washed with acetone (2 x 75 ml). The organic solutions were combined and the solvent removed. The fulgide (5, X = 2,5-dimethyl-3-thienyl) (both isomers) was crystallised from 2-propanol. Yield 26.5 g.

CLAIMS

1. A photoactive compound having the general formula



(III)

in which

A represents oxygen or NR¹ wherein R¹ represents hydrogen, alkyl having 1 to 20 carbon atoms, cycloalkyl having 5 to 12 carbon atoms, aralkyl having 7 to 9 carbon atoms, aryl having 6 to 14 carbon atoms, which may be substituted with one or more halogen or alkoxy groups having 1 to 20 carbon atoms, or alkaryl having 7 to 22 carbon atoms;

P¹ represents a 5-substituted 3-furyl, 3-thienyl, or 3-pyrryl group, said 5-substituted 3-furyl, 3-thienyl and 3-pyrryl groups being unsubstituted or substituted in the 2-position, said optional 2-substituents being selected from alkyl groups having 1 to 20 carbon atoms and aralkyl groups having 7 to 12 carbon atoms, and said 5-substituents being selected from (i) aryl groups having

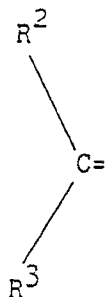
5 to 14 carbon atoms, substituted with a group of the formula $-NR_7P_3$ wherein R_7 and R_8 each represent hydrogen or alkyl having 1 to 20 carbon atoms or together with the nitrogen atom to which they are attached represent a 1-pyrrolidine, a 1-piperidine, or a morpholine group, and (ii) heterocyclic groups selected from 2-thienyl, 3-thienyl, 2-furyl and 3-furyl groups, said last-mentioned 2-thienyl, 3-thienyl, 2-furyl and 3-furyl groups being unsubstituted or substituted by one or more C_{1-3} alkyl groups or halogen atoms;

P^2 represents alkyl having 1 to 20 carbon atoms, cycloalkyl having 3 to 12 carbon atoms, aralkyl having 7 to 9 carbon atoms, aryl having 6 to 14 carbon atoms which may be unsubstituted or substituted with one or more halogen atoms, or alkaryl having 7 to 22 carbon atoms; and

$F>C=$ represents a substituted methylene group, having at least two carbon atoms.

2. A compound according to Claim 1 wherein $F>C=$ has from 2 to 20 carbon atoms.
3. A compound according to Claim 1 or Claim 2 wherein $F>C=$ is a hydrocarbyl radical.
4. A compound according to Claim 1 or Claim 2 wherein $F>C=$ is a substituted hydrocarbyl radical, having one or more substituents selected from hydroxy, oxo, halogen, $-SO_3H$ and $COOH$.

5. A compound according to Claims 1 to 4 in which $F>C=$ has the structure



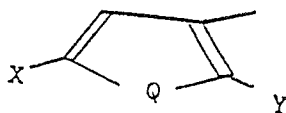
in which R^2 and R^3 independently represent hydrogen, C_{1-20} alkyl, C_{6-14} aryl, C_{7-12} alkaryl, C_{7-12} aralkyl, C_{3-12} cycloalkyl, a heterocyclic group containing 5-12 atoms arranged in one, two or three rings (including bicyclic structures) and having at least one hetero-atom selected from N, S and O (with the proviso that R^2 and R^3 are not both hydrogen) or R^2 and R^3 together represent a divalent cyclic or polycyclic hydrocarbyl group.

6. A compound according to Claim 5 wherein one or more of said alkyl, aryl, alkaryl, aralkyl, cycloalkyl, heterocyclic or polycyclic groups representing R^2 and/or R^3 is substituted by one or more substituents as defined in Claim 4.

7. A compound according to Claim 4 wherein the symbols $F>C$ represents

8. A compound according to any preceding claim wherein P^2 represents methyl.

9. A compound according to any preceding claim wherein P^1 represents a group of structure

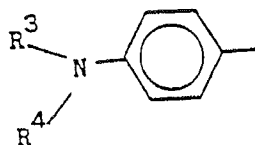


where Q is oxygen or sulfur,

Y is C_{1-4} alkyl

X is selected from:

(a) a 4-substituted phenyl group to the formula



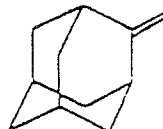
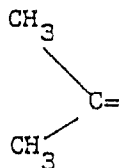
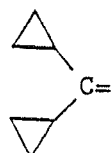
wherein R^3 and R^4 each represents a C_{1-4} alkyl group or together with the nitrogen atom to which they are attached form a pyrrolide, piperidine or morpholine group.

(b) a 2-thiophene group optionally substituted in the 3 and/or 5-position by a C_{1-4} alkyl group.

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- (c) a 3-thiophene group optionally substituted in the 2- and/or 5-position with C₁₋₄ alkyl groups.

10. A compound according to any preceding claim wherein the moieties F>C= are selected from groups of the following formulae:



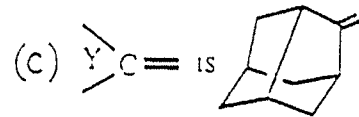
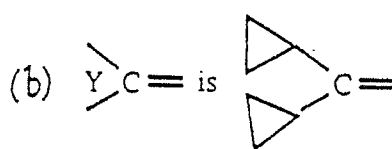
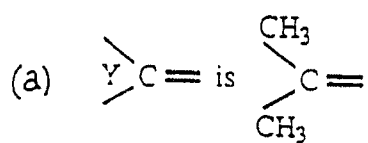
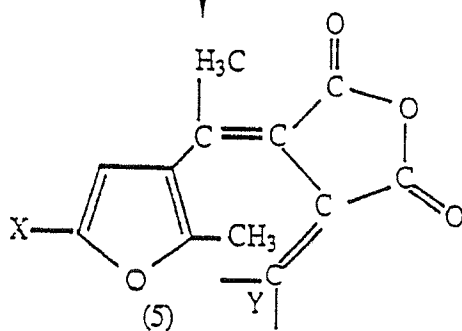
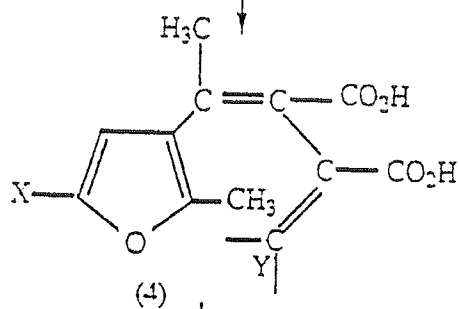
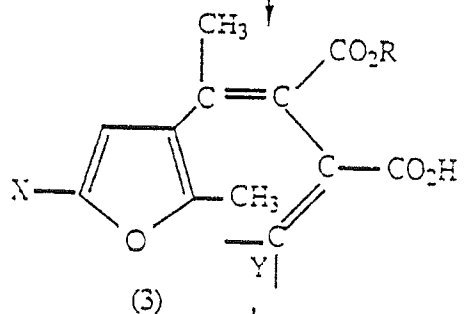
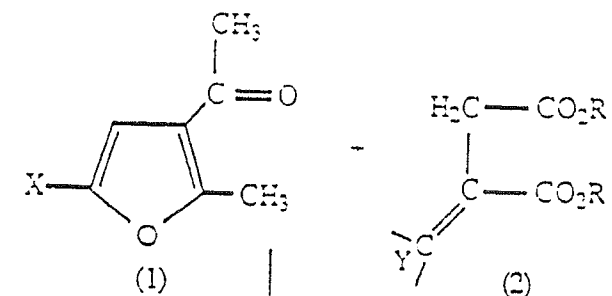
11. A compound according to any preceding claim wherein p¹ represents

5-(p-diethylaminophenyl)-2-methyl-furan-3-yl,
5-(p-piperidinophenyl)-2-methyl-furan-3-yl,
5-(p-pyrrolidinophenyl)-2-methyl-furan-3-yl,
5-(2-thienyl)-2-methyl-furan-3-yl,
5-(3-thienyl)-2-methyl-furan-3-yl,
5-(2,5-dimethyl-3-thienyl)-2-methyl-furan-3-yl,
5-(2-thienyl)-furan-3-yl, or
5-(2,5-dimethyl-3-thienyl)-furan-3-yl.

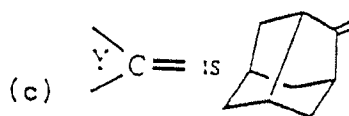
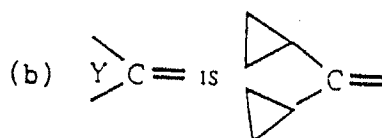
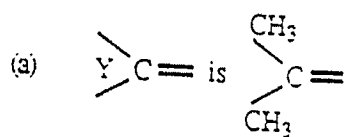
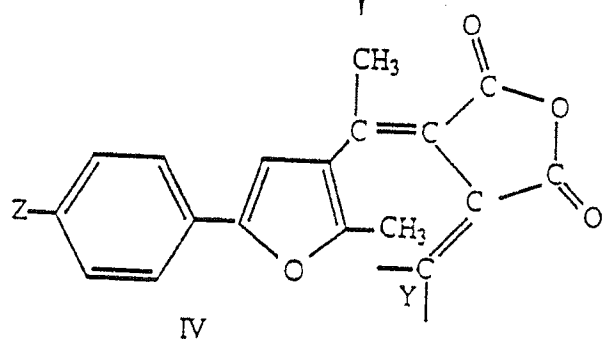
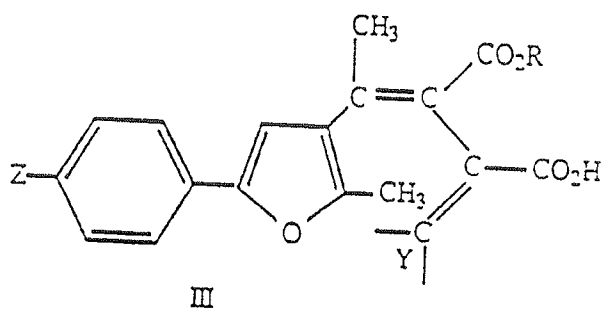
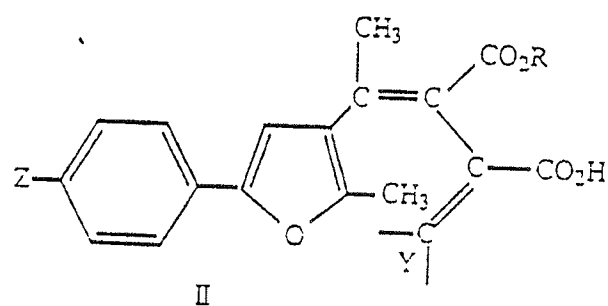
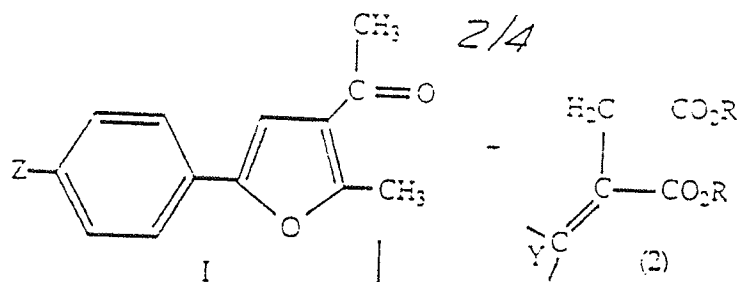
12. A compound according to any preceding claim wherein p² represents a methyl group.

13. Use of a compound as claimed in any of Claims 1 to 11 in the manufacture of image and data recording media.

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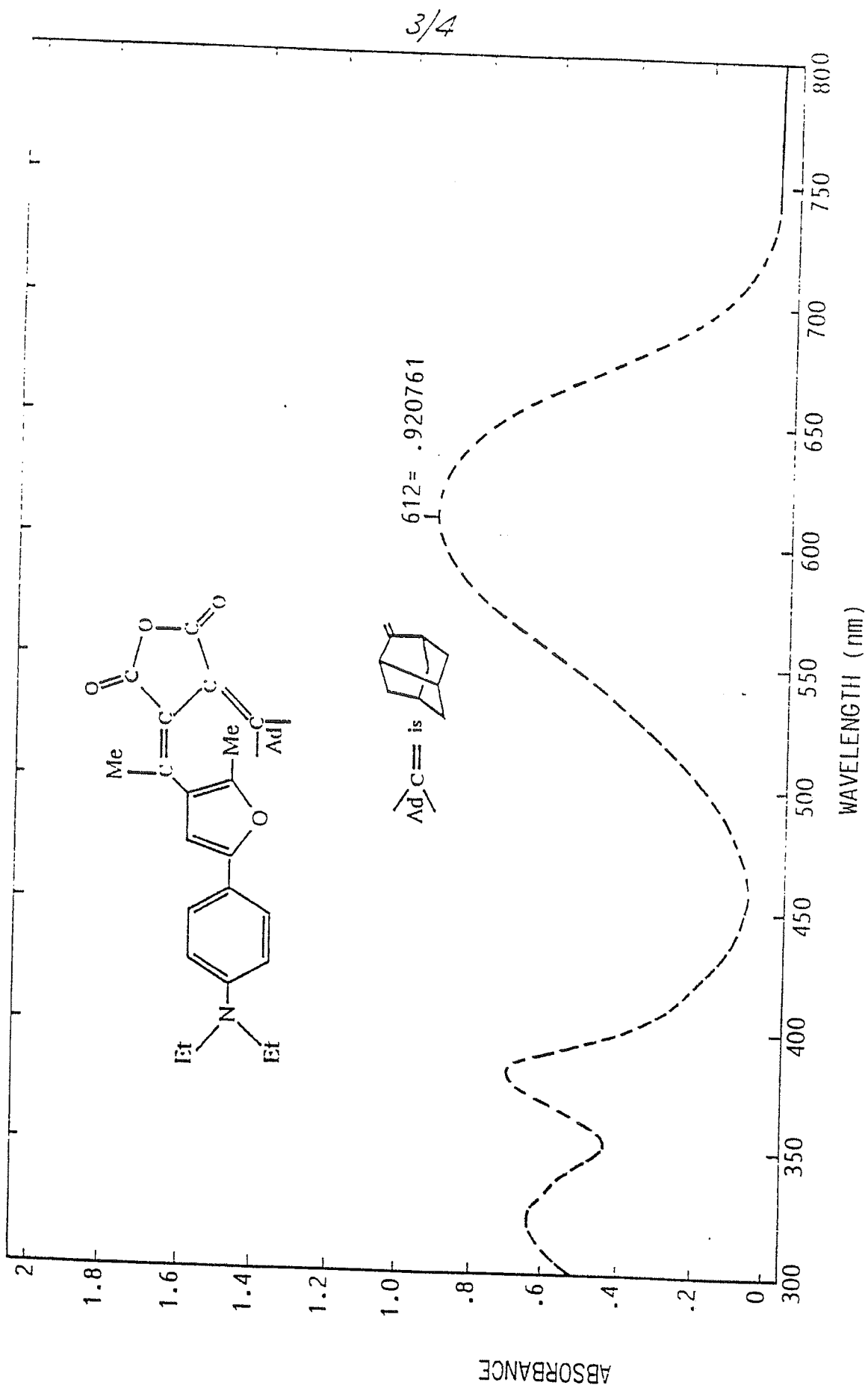


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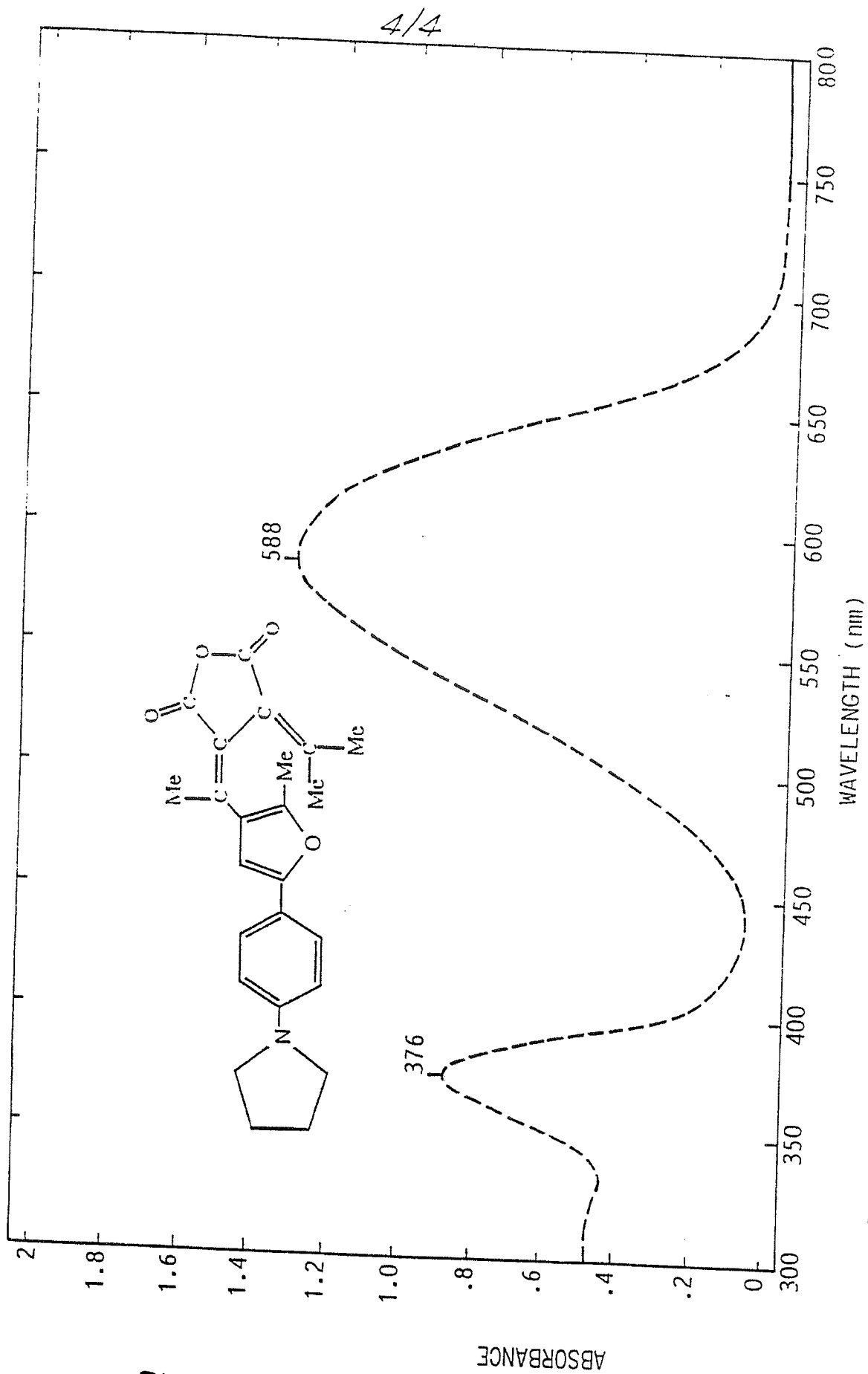


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5x10⁻⁵ M SOLUTION IN TOLUENE AFTER IRRADIATION AT 366 nm TO THE PHOTOSTATIONARY STATE



5x10⁻⁵ M SOLUTION IN TOLUENE AFTER IRRADIATION AT 366 nm TO THE PHOTOSTATIONARY STATE

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INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 90/01118

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC⁵: C 07 D 307/02, 409/14, 207/02, 405/06, 409/06,
G 03 C 1/733

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷

Classification System ¹

Classification Symbols

IPC⁵

C 07 D 307/00, 409/00, 405/00, 207/00

Documentation Searched other than Minimum Documentation
to the extent that such Documents are included in the Fields Searched *

III. DOCUMENTS CONSIDERED TO BE RELEVANT *

Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	DE, A, 2647850 (H.G. HELLER) 2 March 1978 see the whole document --	1-13
P,X	EP, A, 0334477 (TRAQSON) 27 September 1989 see the whole document, particularly examples 15-17 and 19-22 (cited in the application) -----	1-13

* Special categories of cited documents: ¹⁰

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"A" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

25th October 1990

Date of Mailing of this International Search Report

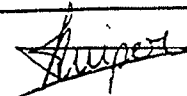
20 NOV 1990

International Searching Authority

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Mme N. KUIPER



ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.

GB 9001118
SA 38805

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 12/11/90
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A- 2647850	02-03-78	FR-A- 2363568	31-03-78
		JP-A- 53031656	25-03-78
		NL-A- 7611809	02-03-78
EP-A- 0334477	27-09-89	AU-A- 3284989	06-09-89
		WO-A- 8907597	24-08-89